

Alkylene Carbonates as Water Glass Cure Accelerants

Field of the Invention

The present invention relates to the curing of cementitious mixtures. More particularly it relates to the curing of cementitious systems which contain sodium silicate, and to cure rate accelerants useful in such systems.

Background Information

It is known that alkylene carbonates such as ethylene carbonate, propylene carbonate and butylene carbonate, (hereafter referred to as EC, PC, and BC, respectively) enhance the rate of curing of aqueous sodium silicate, e.g. water glass, in the application of their use in foundry sand binders in the manufacture of various molded objects. The degree of cure enhancement is dependent on the type of alkylene carbonate employed. For instance, the order of enhancement observed for the aforementioned alkylene carbonates is: EC > PC > BC, i.e., ethylene carbonate causes a more rapid cure of a given system on an equimolar basis than do either propylene carbonate or butylene carbonate. This difference in the reactivity of substituted alkylene carbonates lends itself well for advantage to be taken in that blends of EC and PC or PC and BC can be prepared that exhibit varying degrees of cure enhancement over a wide range. In this way, the foundry industry can easily obtain binder formulations that provide ideal working times specific to particular processes or environmental conditions.

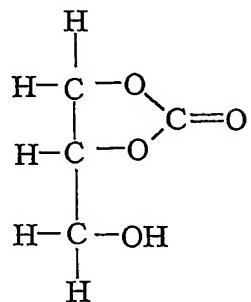
However, the use of carbonate blends in foundry applications has a disadvantage related to their freezing point. Although PC and BC have freezing points below -40° C,

EC will freeze at temperatures below 36° C. For this reason, the use of EC or EC/PC blends that are rich in EC is problematic if fast curing is desired.

The present invention provides novel mixtures of commercially available alkylene carbonates that exhibit fast curing of water glass yet themselves freeze at sufficient low temperatures to enable their employment.

Summary of the Invention

Glycerine carbonate has the structure:



One embodiment of the present invention involves a process for causing curing of an aqueous solution containing a water-soluble silicate by addition of a liquid catalyst mixture comprising an alkylene carbonate to the aqueous solution, wherein the alkylene carbonate is selected from the group consisting of: ethylene carbonate, propylene carbonate, and butylene carbonate, and mixtures thereof, wherein the improvement comprises including an effective amount of glycerine carbonate in said liquid catalyst mixture to render said liquid catalyst mixture to have a freezing point that is below about 15 degrees centigrade, and preferably below about 0 degrees centigrade.

Detailed Description

The problems associated with the use of sodium silicate cure accelerators that contain EC stemming from the relatively high freezing point of EC are alleviated by the instant discovery that mixtures of PC and another alkylene carbonate known as glycerine carbonate (hereafter "GC") accelerate the cure of sodium silicates to about the same extent as does pure ethylene carbonate. However, unlike EC, GC does not disadvantageously freeze at temperatures above

-40° C. Thus, the invention provides blends of GC and PC that offer a wide range of curing times to the industry, while retaining liquid-state status over a broader temperature range than the cure accelerators of the prior art.

It is known that the reactivity of alkylene carbonates with amines follows the order: EC > PC > BC. Thus, the prior art teaches that the reactivity of the carbonates with amines decreases with the size of the substituent attached to the carbonate ring, and one of ordinary skill would naturally expect that GC should possess a relative reactivity somewhere between PC and BC, based on substituent size, given its molecular structure. However, as the data herein show, the reactivity of GC actually lies very close to that of EC in the case of catalyzing the cure of sodium silicate. Cure accelerator blends according to the invention containing GC were found to cure sodium silicate as fast as EC as the data set forth herein shows. This result is unexpected in view of the reaction rate of GC in reactions with other chemical species, such as amines.

The rate of sodium silicate cure in the presence of alkylene carbonates was determined by measuring the time required for the mixture to first show visible signs of gellation following

the addition of the sodium silicate. In all cases, aqueous sodium silicate solution was added to a glass vial containing the desired alkylene carbonate or alkylene carbonate mixture. The resulting mixture was then stirred vigorously with a metal spatula and the time required for the mixture to change from a translucent liquid to an opaque gel was recorded. For each of the examples herein, the weight ratio of sodium silicate solution to carbonate(s) was maintained at 9:1 (10 wt. % carbonate).

Sodium silicate mixtures possessing different ratios of silica (SiO_2) to sodium oxide (Na_2O) were also tested. Relevant properties of the different sodium silicate solution tested are given in the Table I below:

Brand*	$\text{SiO}_2/\text{NaO}_2$ Ratio	Water (wt. %)	Density (g/ml)	Viscosity (centipoise)
1	3.22	62.4	1.38	180
2	3.21	61.7	1.40	237
3	2.40	52.9	1.56	600
4	1.80	62.5	1.44	

Table I

*Brand 1 -PQ Corporation, N[®] Clear

*Brand 2 – Fisher Scientific Products, technical grade

*Brand 3 – PQ Corporation, RUTM, 10% dilution with water

*Brand 4 – PQ Corporation, STARSO[®]

Table II below displays gel times (in seconds) for each of the aforementioned sodium silicate solutions in the presence of EC, PC, BC, GC, and mixtures thereof. Data is given in the format X – Y, wherein X and Y represent the time required to reach the onset of gel and a fully gelled state, respectively. Note that the onset of gel is usually accompanied by an abrupt increase in the viscosity and cloudiness of the mixture, whereas a mixture that ceases to flow under the stirring action of the spatula is considered a gelled mixture. The time required for mixtures to fully harden was not measured. All values are an average of two trials.

Carbonate Component (wt. %)				Sodium Silicate Brand			
EC	PC	BC	GC	1	2	3	4***
100	-	-	-	10-13	13-16	39-61	104-108
	100	-	-	23-29	61-70	> 240	> 240
-	-	100	-	215-234*	> 240	> 240	> 240
-	-	-	100	10-24**	12-30**	14-36**	> 240
25	75	-	-	14-18	26-32	240-260	> 240
50	50	-	-	13-16	12-16	150-164	> 240
75	25	-	-	10-12	12-16	103-114	195-199
-	90	10	-	27-33	81-87	> 240	> 240
-	70	30	-	46-60*	122-130*	> 240	> 240
-	50	50	-	68-82*	182-197*	> 240	> 240
-	95	-	5	18-22	48-54	> 240	> 240
-	90	-	10	16-20	31-39	> 240	> 240
-	80	-	20	10-12	13-22	235-252	> 240
-	70	-	30	10-12	11-16	151-168	> 240
-	50	-	50	< 10	10-15	58-76	> 240
-	25	-	75	< 10	< 10	33-43	> 240
90	-	-	10	< 10	10-14	52-59	102-109
75	-	-	25	< 10	10-14	34-46	107-114
40	-	-	60	< 10	< 10	25-35	> 240
20	-	-	80	< 10	12-20**	19-31	> 240

Table II

* Unlike most mixtures, gellation of formulations containing BC is not accompanied by an abrupt viscosity increase. Rather, gellation occurs over a broader time range.

** Formulations containing significant amounts of GC are not initially compatible, which results in longer than expected mixing times to reach a gelled state.

*** Unlike most mixtures, a slight to moderate exotherm accompanies gellation of all formulations containing sodium silicate brand 4.

It can be concluded from the data in Table II that the general order of cure enhancement due to the presence of added alkylene carbonate is as follows: EC \equiv GC > PC > BC. It can also be concluded that the rate of cure is strongly dependent on the SiO₂ / Na₂O ratio and increases with this ratio. A ratio of SiO₂ / Na₂O greater than 2.4 is required if fast curing is desired. In general, mixtures of GC/PC blends outperformed the analogous EC/PC blends for all but brand 4, which possesses an SiO₂ / Na₂O ratio much too low to promote fast

curing. In addition, EC/GC blends outperformed the analogous EC/PC blends as well. These results are set forth graphically in FIG. 1.